Abstract

Yttria stabilized Zirconia (8YSZ) is an extensively used solid electrolyte, which finds applications in electrochemical sensors, solid oxide fuel cells and gate oxide in MOSFETs. Recent studies report that YSZ thinfilms are better performers than their bulk counterparts, in terms of ionic conductivity even at moderate temperatures. YSZ thinfilms also attract attention with the scope of device miniaturization. However, most of the studies available in the literature on YSZ thinfilms focus mainly on their electrical characterization. In this work, YSZ thinfilms were deposited, characterized and possible use of sensors were evaluated.

In the present work, 8 mol% yttria stabilized zirconia thinfilms were deposited using RF magnetron reactive sputtering under different deposition conditions. Films with thicknesses ranging from few tens to few hundreds of nanometers were deposited. The deposited films were subjected to morphological, structural, compositional and electrical characterizations. Deposition and annealing conditions were optimized to obtain dense, stoichiometric and crystalline YSZ thinfilms. The ionic conductivity of 200 nm nanocrystalline thinfilm was found to be two orders of magnitude higher than the bulk. The ionic conductivity increased with the decrease in film thickness.

Compositional analyses of a set of YSZ thinfilms revealed free surface yttria segregation. The free surface segregation of dopants can locally alter the surface chemistry and influence the oxygen transfer kinetics across the electrode-electrolyte interface. Although number of reports are available on the segregation characteristics in YSZ bulk, no reports are available on yttria segregation in YSZ thinfilm. Hence, this work reports detailed investigations on the free surface yttria segregation in YSZ thinfilms using angle resolved X-ray photoelectron spectroscopy (XPS). Influence of annealing temperature, film thickness, annealing time, and purity on the segregation concentration was determined. It was found that

the most important factor that determines the segregation was found to be the target purity. The segregation depth profile analysis showed that the segregation layer depth was proportional to segregation concentration. Free surface segregation reduced the ionic conductivity of the YSZ thinfilms roughly about a factor. However, segregation did not affect the film's morphology, grain size, crystallinity and activation energy. The difference in ionic conductivity observed in the segregated and clean YSZ films suggests that dopant free surface segregation could also be one of the reasons for the variable ionic conductivity reported in the literature.

For using YSZ in miniaturized devices, micro-patterning of YSZ is important. It has been reported that the wet etching techniques available for YSZ were not repeatable and do not etch annealed YSZ samples. Reactive ion etching (RIE) is better suited for YSZ patterning due to its capability to offer high resolution, easy control and tunable anisotropic/isotropic pattern transfer for batch processing. Although reports are available on the dry etching of zirconia and yttria thinfilms, no studies were reported on the dry etching of YSZ thinfilms. In this work, inductively coupled reactive ion etching (ICP-RIE) using fluorine and chlorine chemistries were employed to etch YSZ thinfilms. Optimized etching conditions were identified by varying different process parameters like, type of gas, gas flow rate, RF power, ICP power, chamber pressure and carrier wafer in the ICP-RIE process. Optimized conditions were chosen by examining the etch depth, composition analyses before and after etch using XPS, selectivity towards SiO_2 (which is the most common buffer layer) and surface roughness. Etch chemistries involved in a particular plasma (SF_6, Cl_2 and BCl_3) were discussed with the help of surface composition and etch thicknesses. The results showed that etching YSZ with BCl_3 plasma at optimized conditions yielded best results through oxygen-scavenging mechanism. A maximum etch rate of 53 nm/min was obtained in BCl_3

plasma using PECVD Si_3N_4 carrier wafer at an ICP power of 1500 W, RF power of 100 W, chamber pressure of 5 mTorr with 30 sccm BCl_3 flow.

Sensing devices were designed by employing YSZ thinfilm as solid electrolyte and nickel oxide and gold thinfilm as sensing and reference electrodes, respectively to evaluate the possible use of YSZ thinfilm in miniaturized NO_2 sensor. The electrodes were deposited in inter-digitated pattern. Two types of electrodes were designed with different number of fingers in symmetric and asymmetric configurations. The NO_2 sensing was performed in the concentration range of 25 to 2000 ppm at three different temperatures, 673, 773 and 873 K in mixed potential and impedancemetric modes. The mixed potential type measurements were carried out only for asymmetric cell in two different electrode configurations. The impedancemetric type measurements were carried out for both symmetric and asymmetric cells in two different electrode configurations. Preliminary NO_2 sensing experiments in both the types of measurements revealed that in devices with electrodes having more fingers were better in performance.

In mixed potential type sensors, sensitivity was measured as the amount of voltage generated when the sensor was exposed to a test gas. The generated voltage was found to be proportional to the logarithm of NO_2 concentration in the entire measurement range (50 to 2000 ppm) with the regression fitting parameter, adj.R^2 around 0.97 to 0.99 in all the cases. A maximum potential of 271 mV was measured with 2000 ppm NO_2 at 873 K. The response and recovery times of the sensors were sensitive to the operating temperature.

In impedancemetric mode, the sensitivities were measured as the variation in the low frequency phase angle ($\Delta\varphi$) when the gas concentration is changed. The frequency range of the measurement was from 0.01 Hz to100 kHz. The response time in the impedancemetric sensors was comparable to that of mixed potential sensors. But the recovery time in impedancemetric sensors was much was slower than the mixed potential type for all the

concentrations. The sensors showed linear response only in a narrow range of 50 to 500 ppm with regression fitting value, R^2 around 0.98 in all the cases. Above 500 ppm, the sensitivity value was observed to be saturated. From the gas sensing studies performed on the miniaturized sensors, it was found that the mixed potential type sensing mode is better than the impedancemetric type in YSZ thinfilm based devices. However detailed interference gas studies were needed before drawing any conclusion.

In summary, the studies presented in the work have contributed to the understanding of free surface yttria segregation behavior in YSZ thinfilms. Micromachining conditions were optimized for both pristine and annealed YSZ thinfilms. Suitability of YSZ thinfilm based miniaturized NO_2 gas sensor was evaluated.